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SCIENCE DIRECT®

Science of the Total Environment 338 (2005) 159–182

Science of the
Total Environment
An International Journal for Scientific Research
into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Nongovernmental valorization of carbon dioxide

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Received 22 January 2004; accepted 23 June 2004

Abstract

Carbon dioxide (CO_2) is considered the largest contributor to the greenhouse gas effect. Most attempts to manage the flow of CO_2 or carbon into our environment involve reducing net emissions or sequestering the gas into long-lived sinks. Using CO_2 as a chemical feedstock has a long history, but using it on scales that might impact the net emissions of CO_2 into the atmosphere has not generally been considered seriously. There is also a growing interest in employing our natural biomes of carbon such as trees, vegetation, and soils as storage media. Some amelioration of the net carbon emissions into the atmosphere could be achieved by concomitant large withdrawals of carbon. This report surveys the potential and limitations in employing carbon as a resource for organic chemicals, fuels, inorganic materials, and in using the biome to manage carbon. The outlook for each of these opportunities is also described.

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Keywords: Carbon dioxide; Managing carbon; Storage of carbon; Carbon storage in biomass and soils; Fuels; Chemicals and minerals

1. Introduction

Ascribing the rise in atmospheric CO_2 concentrations as largely anthropogenic has elicited significant debate within both scientific and political communities. There are questions about whether we even need to manage carbon emissions or even can or choose to manage them. In discussions about carbon sequestration and management, a question that often arises involves whether the greenhouse gases carbon dioxide (CO_2) and methane can be used and valued as sources of carbon rather than as waste emissions and molecules that need to be stored in long-term sinks. While methane is a low-carbon energy source, converting methane to higher value fuels yields CO_2 as an end product. Attempts to couple methane to produce higher value fuels has been ongoing for many years (Srivastava et al., 1992; Villa and Rapagna, 1998; Iglesia, 2002). Reforming methane to hydrogen as a fuel is now being considered as well as its current

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doi:10.1016/j.scitotenv.2004.06.025

use as a chemical feedstock (Choudhary et al., 2001). However, this report focuses on CO_2 rather than methane.

Carbon dioxide has been branded as the primary culprit in discussions about carbon management and climate change. Some argue that this is not clear or that managing carbon will mitigate anything (Cunningham, 2001). This report focuses on the potential to value CO_2 economically and technically as a resource in the context of carbon management as an alternative to relying on governmental valorization to dictate its fate and use. This is an economically driven carbon management model rather than one based on governmental responses to the Kyoto and Montreal protocols to valorize carbon in order to manage carbon emissions.

Ascribing the rise in atmospheric CO_2 concentrations as largely anthropogenic has elicited significant debate within both scientific and political communities. Geologists have made public comment on this topic: “Because no tool is available to test the supposition of human-induced climate change and the range of natural variability is so great, there is no discernible human influence on global climate at this time” (Gerhard and Hanson, 2000). Others have looked at the issue more globally and politically and concluded that the relationship between carbon dioxide and climate change has not been demonstrated (Cunningham, 2001).

The cycles of carbon flows operating on Earth include geochemical and oceanic cycles involving physicochemical diffusion and chemical reactions; biotic cycles involving the biota, soil, and detritus in the soils; and the combustion of fossil fuel, concomitant production of CO_2, and the interactions between these cycles. As the concentration of CO_2 in the atmosphere continues to increase, the feasibility of instituting an alternative cycle wherein the atmosphere is considered a reservoir of carbon to be accessed and used like a bank merits examination. We are clearly making deposits into this atmospheric bank and, aside from the reported increases and changes in biomass growth due to a fertilization effect, we are not making many, if any withdrawals (Bazzaz and Sombroek, 1996; Berendse et al., 2001; Fang and Chen, 2001a). An alternative cycle, which uses CO_2 as a resource, could provide for fundamental societal and infrastructure needs—roads, buildings, chemicals, and fuels. We address aspects of these that can serve as the basis for answering the following questions. Can such anthropogenic withdrawals, driven by economic need and technical capability, provide materials and resources needed to maintain societal growth using the carbon reservoir in the atmosphere? If so, what might be the impact on the carbon budget? Where might the greatest impacts occur and what are the uncertainties in current findings?

Specifically, this paper does not discuss climate change strategies, carbon flows, new approaches to CO_2 capture, increasing energy efficiency to mitigate carbon emissions into the atmosphere, or replacing fossil fuels with renewables or carbon sequestration. Instead, we will discuss carbon uses that could be valued as materials and products. How such processes can be coupled to low-carbon energy sources such as renewable energy (solar, wind, biomass, hydropower, etc.) is briefly discussed. While there are no preset minima for the level of carbon fixed into these commodity products or the level of fossil fuels displaced that would justify this concept, this discussion deals with processes that have the potential to fix carbon into forms that are produced in Tg (one million metric tons) or more quantities and durable products that possess lifetimes for carbon storage of 50–200 years. This is a storage option rather than full-scale sequestration. Given the concerns over deep physical storage systems of carbon dioxide in oceans or mines that could leak or even “bump” to the surface with deleterious effects, storage may be a reasonable alternative to examine, particularly if the storage amounts could be large with 100–200 year lifetimes. Management of carbon in the marine environment is beyond the scope of this report, but some brief references to marine environments will be made in relation to specific opportunities.

The study of C1 chemistry and the use of CO_2 as a reactant predates the debate over the potential impact of increased concentrations of CO_2 on our climate. CO_2 is a desirable carbon feedstock because of its abundance, nontoxicity, and low cost (Inui et al., 1993; Magrini, 1994; Carranza et al., 1999; Noh et al., 2000; Holm-Larsen, 2001; Zevenhoven et al., 2002). Industrially, if CO_2 could be used to introduce C–C, C–O, or even C–X bonds, inexpensive organic syntheses could be facilitated. This rationale has also been successfully adopted by the green chemistry movement, which proposes using CO_2 as a replacement for toxic reagents such as phosgene (McGhee et al., 1993; Anonymous, 1994), a solvent or reaction media in its supercritical state (Abraham and Moens, 2002), or even a mild oxidizing reagent (Noh et al., 2000; Park et al., 2000). In addition, the National Aeronautics and Space Administration (NASA) has a long history of developing bioregenerative life support systems in which the use of CO_2 is an essential part of long-term space habitation scenarios (http://www.qadas.com/qadas/nasa/nasa-hm/0254.html, http://www.advlifesupport.jsc.nasa.gov/, http://www.bio.purdue.edu/nscort/homepage.html and http://www.elflore.org/celsslinks.html). In the NASA examples, integrated bioregenerative life support systems employed hybrid chemical/biological systems to convert CO_2 to methanol and then to a single-celled food source (Stokes and Petersen, 1982; Petersen, 1983). In related work with military applications, reduction of CO_2 to methanol was followed by conversion of the methanol to extracellular polysaccharides by yeasts (Petersen et al., 1989; Petersen et al., 1990). Also for the same applications, hydrogen-utilizing bacteria were used to reduce CO_2 to polysaccharide (Kern, 1985).

The major challenge to using CO_2 as a feedstock is that it lies at the bottom of a thermodynamic well. Nature elevates carbon to energy-rich molecules such as glucose using solar energy and biological catalysts in a low-temperature biological carbon cycle. In the oceans, the geochemistry of CO_2 involves essentially three reactions in differing states of equilibrium involving CO_2 gas, water, H_2CO_3 and the ions of carbonate (HCO_3^{-1}, CO_3^{-2}), calcium, H^+, and other metal ions. This carbon buffer is immense—38,000–39,000 petagrams (Pg) (Baes, 1982; Butler, 1982)—and Butler estimates that the buffering capacity of rock weathering and the oceans far exceeds any reasonable estimate for the amount of CO_2 that would be emitted over the next one or two centuries by fossil fuels (Butler, 1982). However, short-term impacts and changes that appear to be related to increased CO_2 flux into the oceans, such as those observed on coral reefs, can and are occurring (Ver et al., 1999). Thus the geochemical cycles for carbon and its inorganic forms, CO_2 and carbonates, generally exist in a steady state within the terrasphere and oceans, and essentially serve as large storage buffers for all carbon fluxes, albeit on millennial temporal scales. Unfortunately, the impacts of changes in carbon concentrations are also on millennial time scales and not quickly reversed.

Systems analysts have looked at individual systems for their contribution to carbon sequestration and consider them inadequate to meet the ability to manage carbon, citing that a systems approach is needed because there is not a natural “savior” to assimilate the anthropogenically derived carbon (Falkowski et al., 2000). There is also the issue of self-adjusting biomes and whether they can really do much to manage carbon flows.

Using CO_2 as a reactant molecule (carbon source) to deal with overall carbon management must involve very large-scale production processes and more demanding process criteria, i.e., few steps, simple and very low cost. Finally, such an effort will require significant interdisciplinary efforts. There are three potential scenarios that could address the use of CO_2 as a reactant for high-volume products and meet the constraints noted above:

1. Use carbon and CO_2 as a feedstock or precursor to produce long-lasting products such as plastics or as a fuel to displace fossil fuels;
2. Enhance the levels of carbon stored in trees, vegetation, and soils;
3. Use CO_2 in novel inorganic applications.

The paper will discuss the current status of each approach (although not designed to be carbon sinks, they do in fact act as such in their current use), the potential impact on carbon budgets, opportunities to employ these approaches and any ancillary benefits, the limitations or barriers to using these approaches, and finally, the outlook for the future of such approaches. Halmann and Steinberg recently published a comprehensive science and technology analysis of carbon dioxide mitigation (Halmann, 1999). They employed a systematic and useful approach to analyze many of the concepts being proposed to mitigate CO_2 and used common bases—energy and dollar values—to compare concepts. They also provided details on some of the options with some options discussed in more detail than others. This paper complements or expands on some of the information in their book. We take a more rigorous look at some items such as using CO_2 for plastics. Our estimates of the potential for using CO_2 in commodity goods such as plastics very closely match those estimated in Halmann and Steinberg using a systems approach. They also recognized the gap in data related to storing carbon in the biome and we provide some analysis of that option which was an area Halmann and Steinberg called out as a research need.

1.1. Modeling and models

Many published studies relative to carbon budgets, cycling, and sequestration are based on modeling data. Most modeling uses some empirical data. In this report, we avoided basing any of our assumptions and conclusions on pure models as much as possible. We attempted to use actual data or theoretically sound projections based on known chemistries. We cited modeling when model databases contained substantial amounts of empirical data. McGuire et al. (2001) provides a good list of the steps needed to provide models with the kind of data that will allow for better analyses and potential predictive capability.

1.2. Units

We did not differentiate between short and long tons in citing numbers, as many of the citations do not differentiate. Because the numbers are very large, the differences between short and long tons are likely to fall within error bars. Conventionally, we have employed the metric values, tera- and petagrams and where possible have converted cited numbers to such nomenclature. For reference, 1 petagram (Pg) or 10^{15} g is equivalent to 1 gigaton (Gt) or 10^9 metric tons; and 1 teragram (Tg) or 10^{12} g is equivalent to 1 megaton (Mt) or 10^6 metric tons.

2. CO_2 as a source of industrial products and fuels

2.1. Background and current use for production of chemicals

Carbon and CO_2 are currently market commodities and tie up a small but significant fraction of carbon. Table 1 shows the carbon form, its annual consumption in the US, and representative uses (Greiner et al., 1999; Heydorn et al., 2000; Auchter et al., 2002).

Table 1
Direct industrial uses of carbon and carbon dioxide in the United States

Carbon form	Annual consumption in the US (Tg)	Typical uses	Growth rate
Carbon			
Carbon black	1.7	Tires, fillers, plastics	1–2%
Activated carbon	0.17	Water treatment, purification of organics	4–4.5%
Carbon dioxide			
Liquid	8.6	Food industry, carbonation, drugs (i.e., salicylic acid), plastics and steel manufacture, metals processing, alternative cleaning agents to hydro-fluorocarbons, foam blowing agents, etc.	3–4%
Gaseous	39.2	Enhanced oil recovery, urea, precipitated calcium carbonate, others	Flat

The total US consumption of these commodities is approximately 50 Tg. Many of these uses do not embody carbon in long-lived forms. For example, CO_2 used in enhanced oil recovery usually returns to the surface within 6 months to 2 years (Heydorn et al., 2000). Almost all of the carbon black is produced from fossil-based materials and much of the activated carbon is manufactured from biobased materials (wood chips, sawdust, coconut shells, peat). While the carbon resulting from tire wear could be in the soil and biota for long periods of time, most tire carcasses are burned for energy; hence, the lifetime of the carbon in these materials is relatively short. Urethane products such as refrigerator insulation or autoshredder fluff (from demolished vehicles) could store carbon for hundreds of years if landfilled. The fate of the carbon in compounds or materials such as urea, medicinals, or plastics will vary depending on use and disposal conditions.

A comprehensive review of the relevance of catalysis to carbon management indicates that worldwide 110 Tg of CO_2 is used annually in chemical synthesis to produce urea, salicylic acid, cyclic carbonates, and polycarbonates (Arakawa et al., 2001). The report also describes 17 potential chemical transformations to reduce CO_2 to chemicals and polymers. While most reactions consist of insertions into simple X—H bonds (amines, P—N, etc.) or more complex O—H bonds, other more complex reductions also occur. Numerous research efforts cited in this review describe a wide range of polymer syntheses including a 12-electron reduction process leading to polyethylene.

2.2. Potential impacts and opportunities for organic chemicals from CO_2

Magrini and Boron (1994) estimated that replacing the entire production capacity of organic chemicals from CO_2 would impact 1% of carbon-based emissions. A more robust analysis can provide some realistic estimates of the potential. The average mole percent carbon contained in 30 large-volume industrial chemicals, ranging from vinyl chloride and urea (~20 mol% C) to benzene (92 mol% C), is about 64–65 mol% C.[1] This makes storing carbon in chemically derived materials such as plastics attractive compared to biomass, which contains only 51 mol% C. In addition, these chemicals can be used in fairly long-lived products such as houses, furniture, fixtures, and household appliances that may have lifetimes of 50 years or more, particularly if landfilled at the end of their useful lives. Table 2 lists the annual volumes of materials that typically end up as these kinds of items in the US (C & EN, 2002). Applying the mole fraction derived above shows that if chemicals and plastics could be manufactured from CO_2, the potential exists to store or manage about 23 Tg of carbon annually. For comparison, the total annual US municipal solid waste disposal mass is about 180 Tg. Worldwide, the total carbon in vegetation is typically cited as about 500,000 Tg.

Table 2
Potential carbon content of various industrial materials if CO_2 were used as the sole carbon source

Item	Lb (millions)	Tgs
Plastic materials	67,750.00	30.8
Synthetic rubber	2230.00	1.0
Noncellulosic fibers	8536.00	3.9
Cellulosics	235.00	0.1
Paints and coatings	1266.00	0.6
Total Tgs		36.3
Total Tgs C		23.4

Manufacturing plastics or other materials from CO_2 is theoretically possible if the CO_2 can be activated to formaldehyde or methanol precursors, for example. It simply requires energy and electrons to reduce the carbon. In the following example, mass and energy balances are included in the process concept. The results illustrate the need for significant advances in both chemistry and very low or no carbon forms of energy to be feasible.

During the last decade, developing a new type of polymer, which is an aggregate of two simple chemicals produced commercially from urea, i.e., cyanuric acid (CA) and melamine (M), has been investigated. Simple mixing of these two chemicals at ambient temperature causes the formation of an ‘aggregate’ (CA–M) that is hydrogen-bonded in a geometrically well-defined and thermally stable structure. However, a basic calculation of the CO_2 balance for this process indicates that there is an overall net production of CO_2. Most of the CO_2 production arises from the high temperature NH_3 production that is required to make the urea. Remaining emissions come from the high temperature/high-pressure process for urea synthesis from CO_2 and NH_3. An overview of the calculations is shown in Table 3. The actual net CO_2 emission is 0.5 kg mol $CA–M^{-1}$.

2.3. Future potential for producing chemicals from CO_2

Industry currently employs carbon in processing and manufacturing. A modest amount of that volume is already stored in somewhat long-lived materials in the case of carbon black or carbon fibers. These

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[1] The chemicals include caprolactam, adipic acid, propylene and ethylene oxide, terephthalic acid, acetic acid, isobutylene, acrylonitrile, phenol, styrene, acetone, xylenes, ethylene glycol, butadiene, cyclohexane, ethylene dichloride, cumene, ethyl benzene, benzene, methyl tertbutyl ether, formaldehyde, methanol, urea, ethylene, propylene, vinyl chloride, toluene, ethyl alcohol, isopropanol, and acetone.

Table 3
Net carbon dioxide emissions profile for a potential production of mixed polymer using carbon dioxide[a]

Product	Number of moles	CO_2 consumption (kg)	CO_2 emission (kg)
NH_3	18		0.55
Urea	9	0.23	
Cyanuric acid (CA)	1		0.14
Melamine (M)	1		0.14
Polymer CA–M	1	–	–
Net CO_2 produced (saved)			+0.59 kg mol polymer^{-1}

[a] The production of 1 mol of CA–M polymer requires a total of 9 mol of urea (i.e., 3 mol of urea for CA, and 6 mol of urea for M). These 9 mol of urea can be generated from 18 mol of NH_3. Using industrial reference data, we calculated that the production of 18 mol NH_3 via steam reforming of CH_4 produces 0.55 kg CO_2. Alternatively, the formation of 9 mol of urea (according to the Mitsui Toatsu process) consumes about 0.23 kg CO_2. Therefore, the net balance is an emission of 0.32 kg CO_2 to generate those 9 mol of urea (from CH_4 and N_2). Using all the data on utility requirements for generating cyanuric acid (CA) and melamine (M), we calculated that the formation of 1 mol CA from 3 mol of urea emits 0.14 lb CO_2, while the formation of 1 mol M also emits 0.14 lb CO_2 from utilities. Since the polymerization of CA with M apparently does not require any external energy input, the conversion of 9 mol of urea into 1 mol of the CA–M polymer is accompanied by a total emission of 0.27 kg CO_2. Therefore, the total emission is 0.59 kg CO_2/mol CA–M polymer, which is 2.3 kg CO_2/kg CA–M.

markets also possess modest economic growth rates. Additional increases in the use of carbon black or activated carbon could have a measurable impact on carbon management. However, a mass and energy balance is needed to determine if net carbon storage actually occurs.

The conversion of CO_2 into durable manufactured goods via high energy thermochemical processing is not a likely means of managing carbon. The simple analysis in Table 3 highlights the largest energy consuming and CO_2-producing steps. If other forces such as carbon taxes or environmental drivers were to push for low CO_2-emitting processes, research could be directed to these obvious high carbon emission sources. For example, new catalysts to conduct the Haber process (reduction of nitrogen to ammonia) under much milder conditions would be required. Also, the formation of urea under milder conditions, i.e., at pressures below 200 atm and temperatures below 180–200 °C, could bring the net CO_2 consumption to 0.03 kg mol urea^{-1} (up from 0.02 kg), if appropriate catalysts could be found.

2.4. Background and current use of CO_2 for production of fuels

In this proposed economically driven carbon management model, fuels are not long-term storage media. However, the potential impact of displacing a fossil fuel CO_2-emitting process with a process in which the combustion products can be recycled into new fuels is high.

Today, there are no large-scale commercial processes that intentionally employ CO_2 as a feedstock for fuels. There are low-pressure processes to produce methanol over Cu, Zn, and Cr oxide catalysts from both CO_2 and CO but these are in limited use (Davenport, 2002).

2.5. Potential impact and opportunities for CO_2-based fuels

About one-third of US emissions originate from transportation fuels. Use of CO_2-based fuels could make this segment of the market carbon neutral and hence significantly mitigate the rise of carbon CO_2 into the atmosphere. Whereas the use of CO_2 for chemicals yields carbon storage potential at Tg levels, the fossil fuel displacement potential for CO_2 derived fuels is on the Pg level.

There is extensive literature on use of C1 compounds as sources for fuels, particularly methane. The potential for producing fuels from CO_2 has also been examined as outlined in the review by Marks (Arakawa et al., 2001). Producing simple fuels such as methanol from photocatalytic or photoelectrocatalytic processes is one area of research.

Most all of the chemistry related to use of CO_2 for conversion into chemicals is applicable to use of CO_2 as a fuel. For fuel products, reactions of CO_2 to form polymer linkages are not as important as the simple electron transfer reactions that achieve the desired reduction processes. Intermediate reduction of CO_2 to carbon monoxide is also a step that can lead to both fuels and chemicals via Fischer-Tropsch chemistry (Mills, 1988, 1993). For fuels production, availability of inexpensive electrical energy or hydrogen is very important for the chemistry and economics of future processes.

A wide range of reducing agents have been examined for their potential to produce fuels from CO_2. These include methane, hydrogen, and electrons via electrochemistry. Direct reforming of methane with CO_2 has been examined but there are several technical barriers and thermodynamically the process may also be a net producer of CO_2 (Seshan et al., 1994; O'Connor and Ross, 1998). Barriers include catalyst development and selection, and process issues such as catalyst coking.

Decarbonization of methane or other hydrocarbons is another approach to obtaining hydrogen from carbon sources. The current commercial process for producing hydrogen, which is based on reforming of hydrocarbons, is a net producer of CO_2. In contrast, decarbonization generates carbon black, which could be stored more easily than gaseous CO_2. The economics and technical feasibility of these processes are still in the early stages of development (Halmann, 1999; Dahl et al., 2001, 2002; Muradov, 2001).

2.6. Limitations to producing fuels from CO_2

Any method of reducing CO_2 in the atmosphere will require energy. Novel approaches such as using solar electricity and wind may provide some options for the future. Using the electrical energy from these intermittent power sources to produce a fuel from CO_2 can be envisioned as an energy storage strategy.

Electricity from nuclear power plants may also be a source of reducing electrons. While this source of electrons can be relatively inexpensive, there are some perceptual issues with this approach regarding environmental impacts. Nonetheless, it is an approach that yields very low carbon emission profiles. The call for improved catalysis is often proposed as a means of achieving cost-effective and efficient conversion. Catalyst research moves ahead, although not as many resources are devoted to this specific area in the US as in other countries (Magrini and Boron, 1994).

2.7. Outlook for use of CO_2 as a raw material for fuels

The driving factors that might move the transportation industry to employ CO_2 as a feedstock for fuels production will likely be environmental. However, those in policy-making positions do not feel the need for that driver has been clearly shown; hence, the outlook for this approach tends to remain a research-level effort in the US. In contrast, other countries with limited access to fossil fuels tend to view CO_2 as a real resource and commit government resources to develop such efforts. The move to a hydrogen economy is another driver that seems to be pushing for the use of carbon with a concomitant storage potential. Obtaining hydrogen from carbon-based materials is a transition strategy. Whether this approach yields some potential to manage carbon or creates issues with excess carbon emissions is yet to be determined.

3. Managing, employing and enhancing the levels of carbon stored in trees, vegetation, and soils

3.1. Background and current use

The simplicity of nature's storage mechanism for carbon in terrestrial ecological systems (exclusive of geologic formations) suggests that we might be able to leverage these natural mechanisms and employ them for the purpose of managing carbon. The carbon in these sinks possess lifetimes on a century time scale, although most soils may have forms of carbon that range from transient to persistent depending on the depth of the soil horizon and age. These storage media also meet the criteria defined above for economically driven carbon cycling relative to lifetimes, use, and economic value for a growing population. The question is whether we can manage any of these carbon flows to truly have any impact on carbon budgets in the atmosphere. The following discussion is based on a sampling of the volumes of literature that address the issue of carbon storage and lifetimes within terrestrial ecosystems. It is intended to highlight issues rather than be comprehensive.

A recent paper addressed the state of the recent patterns and mechanisms of carbon in terrestrial ecosystems and compared carbon budgets for the last two decades of the 20th century (Schimel et al., 2001). The data summarized below are based on estimates of emissions of carbon in the 1990s made by the International Panel on Climate Change.

Values with a negative sign represent removal from the atmosphere.

Terrestrial ecosystem	Carbon content (Pg year^{-1})
Fossil fuel burning and cement	6.3±0.4
Atmospheric increase	3.2±0.1
Ocean–atmosphere flux	−1.7±0.5
Land–atmosphere flux	−1.4±0.7
Emissions due to land use changes	Assume 1.6±0.8
Residual terrestrial sink	−2 to −4 (highly uncertain)

Ecosystem dynamics and the inability of the scientific community to predict or even fully assess such dynamics has been called out as a major hurdle in using natural systems as means to manage carbon (Breshears and Allen, 2002). However, the ebb and flow of carbon need not be dramatically altered to achieve some measures of carbon storage. Small increments over wide areas could have significant cumulative effects. If these effects are relatively short-lived, viz. 50–200 years, they may not impact the very long-term carbon stock issues, but they may be attractive in the near and midterm to ameliorate some ancillary side effects of localized high CO_2 concentrations.

Consideration of forests as carbon sinks has been extensively studied. The United States Department of Agriculture (USDA) is tasked with preparing periodic reports on the forest resources within the US. A recent study addressed the influence of elevated CO_2 on plant productivity, and the development of models used to explore the potential impact on forests, wood products and carbon in the US. (Joyce and Birdsey, 2000). It also provided a snapshot of the existing conditions and current impacts of forests on actual and potential carbon storage opportunities.

The USDA reported that the carbon stored in forests, in wood and paper products in use, and in dumps and landfills is increasing and is large, accumulating to a level of 2.1 Pg since 1910 (Skog and Nicholson, 1998; Joyce and Birdsey, 2000). Comparatively, the carbon inventory in forest trees amounts to 13.8 Pg with 24.3 Pg in understory, floor, and soils. Individual regions within the US have been analyzed to provide specific regional data over finite time periods, resulting in regionally specific valuation of carbon storage. Table 4 presents some of the data being gathered and analyzed to characterize regional or specific biomes. While not comprehensive, it provides a brief look at the breadth of analyses being undertaken to assess this storage potential as well as the variety of methods used to make these assessments.

In the summation of IPCC data shown above there is an assumption that, overall, land use changes add carbon to the atmosphere. However, the carbon attributed to land use changes may be more greatly impacted by climate (precipitation and temperature) than by change of use (Clair et al., 1999; Chapin et al., 2000; Tian et al., 2000; Houghton, 2000; Yang et al., 2001). Shimel notes that 10%–20% of the carbon fixed by plants in the northern extratropics in the 1990s remained in the biosphere, which correlates with other inventory studies that show that re- and afforestation occurring in these same latitudes is partly due to intensive management or recovery from disturbances (Schimel et al., 2001; Goodale et al., 2002). In one analysis, land use changes in the United States were estimated to accumulate carbon at the rate of 300–400 Tg C year^{-1} in 1980, once fire and fire management analyses were included (downward from earlier estimates) (Houghton and Hackler, 2000; Houghton et al., 2000). Carbon emissions or sinks resulting from land use and from offsetting fossil fuel emissions (Houghton et al., 1999) have also been estimated. These estimates are being further refined as better data are obtained from specific sites. Some showed no lasting (deleterious) effects on soil carbon but rather increases in soil carbon content, although ecosystem carbon was impacted (Johnson and Curtis, 2001; Johnson et al., 2002). Hence, terraspheres are acting as carbon sinks but quantifying the magnitude has been a challenge due to the large number of variables involved, such as land use changes and fire suppression (King, 2000; Tilman et al., 2000).

Table 5 summarizes the potential sink values of specific regions or biomes throughout the world and/or the annual rate of carbon storage by the specific biome. Again, the breadth and range of analyses indicates the interest in quantifying these potential storage sinks. For example, although typically not considered as sources of wood products, the urban forests represent a commercial product, albeit one

Table 4
Estimates and measurements of carbon storage in soils and biomes

Biome or ecological area and time span (if applicable)	Potential for soil carbon storage, if estimated	Potential or measured annual rate of soil carbon storage	Overall findings	Reference and method
Rangeland, Midwestern USA		1–300 kg C ha^{-1} $year^{-1}$—dry and warm regions 5–800 kg C ha^{-1} $year^{-1}$—cold and humid regions	Improved agricultural practices can provide increases in SOC in farmland.	(Lal, 2002)—Other referenced reports and estimating the inputs and outputs of agricultural practices.
Forest land, Southeastern US 1953–1997	45.5 Tg C accrued bt afforestation, but 126 Tg C emitted	1 Tg C accrued 2.9 Tg C emitted	A methodology was developed that provided a forest soil estimate. Afforestation added little mineral C to soil. Land use changes had larger impact.	(Heath et al., 2002)—Employed State Soil Geographics (STATSGO) soils database.
Rangelands in US Great Plains		19 Tg C $year^{-1}$—potential mitigation gains 43 Tg C $year^{-1}$—potential avoided losses	Rangelands can be a valuable carbon sink. Improvements in management and managed grazing provide potential means to store carbon.	(Schuman et al., 2002)—Estimated rates based on some gravimetric C and N content in 10 cm of soils at two sites and literature data. Used NRCS, BLM, and USFS acreage estimates.
Small gauged headwater watershed (Maryland)	Overall capacity increased 200–300 ton C ha^{-1}	1.6–2.2 ton C ha^{-1} $year^{-1}$	Larger rates and capacity observed compared to previous estimates. Carbon in histosol had mean residence times of 600 BP.	(McCarty and Ritchie, 2002)—Soil core samples, ^{137}Cs and ^{14}C dating.
US farmland. Considers C sequestration in soil, and emissions from agricultural inputs and machinery		−189 kg C ha^{-1} $year^{-1}$ net flux for all three crops. −468 kg C ha^{-1} $year^{-1}$ relative net C flux[a]	Method allows for estimate of net flux as an absolute value, but also provides an estimate of relative net flux or the full value of a change in land use or other agricultural practice. Changes in practice impacted potential for soybean and cornfields to store carbon. Wheat was a net emitter.	(West and Marland, 2002)—New full carbon cycle methodology, US national average values of agricultural inputs, and changes in tillage practices for corn, wheat, soybean.
Semiarid mixed grass and short-grass rangeland		19 Tg C $year^{-1}$	Grazed soils had more total C than ungrazed lands likely due to more rapid annual shoot turnover and changes in plant species composition.	(Schuman et al., 2002; Reeder and Schuman, 2002)—Gravimetric analysis of top 10 cm of soil, estimates of rangeland condition and acreages from NRCS, BLM, and FS[b].
Tidal salt marshes in the Bay of Fundy—past 30 years		Accumulation rates: outer bay—76 g C m^{-2} $year^{-1}$ Upper bay—184 g C m^{-2} $year^{-1}$.	Soil C density inversely proportional to accumulation rates.	(Connor et al., 2001)—Spatial and temporal sampling of tidal salt marshes of the Bay of Fundy and estimate carbon storage potential.

[a] Total difference between conventional and no till practices.

[b] National resources conservation service, Bureau of Land Management and the United States forest service.

Table 5
Estimated carbon sink and annual rate values of various regions of the world

Sink value	Annual value	Time period measured	Area examined	Citation and methods
44–89 Pg	0.5, 0.9 Pg C year^{-1}	1901–1995	All terrestrial biosphere	(Yang et al., 2001)—Empirical data from soil respiration data
	0.68±34 Pg year^{-1}	19 years—1981–1999	Eurasian boreal and North American temperate forests Canadian boreal forests above 30th parallel	(Myneni et al., 2001)—Data from remote-sensing spacecraft and forest inventories to identify the size and location of such sinks
	0.6–0.7 Pg year^{-1}	1990s	Northern Hemisphere	(Goodale et al., 2002)—Forest inventory information, allometric relationships, and supplementary data sets and models
	0.2–0.5 Pg year^{-1}		North American Forests above 15° latitude	(Chen et al., 2000)—Integrated Terrestrial Ecosystem C-budget model (InTEC)
0.7 Pg	0.02 Pg year^{-1}	Within last 2 years	Urban forests in 10 cities	(Nowak and Crane, 2002)—Sampling in 10 cities and then extrapolated to the US as a whole
0.3–0.58 Pg	0.37–0.71 Pg year^{-1}	1980–1989	Coterminous US	(Pacala et al., 2001)—Inventories, land use changes, ecosystem models
0.45 Pg (since the mid-1970s)	0.021 Pg year^{-1} uptake and a −0.022 Pg year^{-1} emission rate	Since mid-1970s (overall study covered seven periods from 1949 to 1980)	China	(Fang and Chen, 2001a)—Improved estimation method of forest biomass and a 50-year national forest resource inventory (National Forest Resource Inventory Database)
0.71±0.34 ton ha^{-1}		Over past few decades	South America	(Phillips et al., 1998)—Long-term monitoring of plots in mature humid tropical forests
54 Pg		1993–1999	Russia	(Shvidenko et al., 2000)—Estimated from calculations of land areas and data on stocks of biomass
	4.4 Pg year^{-1} NPP	1988–1992	Russia	(Shvidenko et al., 2001)—Estimated using average NPP densities and land area estimates
0.7 Pg		1994	Coterminous US	(Graham, 1994)—Potential for short rotation woody crops and herbaceous crop to be grown for bioenergy applications. Employed stringent criteria for land availability. Value derived from Graham's data
	1.0–2.2 Pg C year^{-1}	1988–1992	Global	(Fan et al., 1998)—Atmospheric CO_2 data since 1988 and two atmospheric transport models
	1.7±0.5 Pg C year^{-1}	1988–1992	North America south of 51 degrees north	(Fan et al., 1998)—Atmospheric CO_2 data since 1988 and two atmospheric transport models
	0.1±0.6 Pg C year^{-1}	1988–1992	Eurasia–North Africa	(Fan et al., 1998)—Atmospheric CO_2 data since 1988 and two atmospheric transport models

Table 5 (*continued*)

Sink value	Annual value	Time period measured	Area examined	Citation and methods
Total: 2.8 Pg (vegetation), 26 Pg (soils), weighted area density: 23 Mg C ha^{-1} (vegetation), 213 Mg C ha^{-1} (soil)		NA	Northeast China	(Wang et al., 2002)—Fourth national forest inventory (122 plots) and second national soil survey (388 soil profiles) and extrapolations based on use of Geographic Information System
285–2950 kg C ha^{-1}		Growing season measurements 1996–1998	Regional forest in central Maine	(Sievering et al., 2000)

Positive values indicate sinks; negative values indicate emissions to atmosphere.

designed to address aesthetic or landscaping needs, but nonetheless a commercial product that stores carbon for 50–200 years.

The impact of wood products on the carbon balance in the US should not be underestimated. In 1990, wood products that were manufactured in the US contained about 147 Tg of carbon. Much of this carbon is contained in durable building products that have a useful life of more than 50 years and often the end site for such materials is a landfill. Recent data suggest that the enzymatic conversion of lignin-rich biomass, e.g., wood, newsprint, brown papers, is very slow, and that more than 70% of the carbon in these materials remains in the landfill indefinitely (Micales and Skog, 1997).

3.2. Potential impacts and opportunities

The carbon sequestration impact of whether to harvest a tree and how best to use that tree is very complex. It is a function of the tree's growth rate, how the biomass will be used, and the time period over which the calculation is made (boundary conditions).

The interactions between the forest growth rate, energy displacement, and harvest time have been extensively studied (Marland and Marland, 1992; Nabuurs, 1996; Price et al., 1996; Marland et al., 1997). Because of the wide range of variables, there are difficulties in drawing sweeping conclusions. Often an "energy displacement factor" is defined in terms of how the biomass is used in producing energy to displace fossil energy or for manufacturing a product. The use of short rotation woody crops or tree plantations as sources of fuel for biomass-to-energy facilities has been evaluated with respect to the impacts of displacing fossil fuels (Marland et al., 1997; Marland and Schlamadinger, 1997; Tuskan and Walsh, 2001). Biomass used to produce wood products for housing and construction will sequester three to eight times more carbon than similar steel or concrete products (Nabuurs, 1996; Price et al., 1996; Trusty and Meil, 1999). These calculations include the carbon emissions from the manufacturing process as well as the carbon in the product. Biomass used for production of short-lived paper products can either be burned for energy production or disposed of in landfills (Skog and Nicholson, 1998). Based on these studies, it seems that biomass has the greatest potential for storing carbon when it is used for durable building materials, rather than for energy production through combustion or for production of nondurable products. However, determining the best use of biomass is complicated by the differences in biomass quality and the current technology, which requires most durable wood products to be made from larger older trees. Even with these complexities, Nabuurs (1996) showed that when fossil fuel displacement is considered, harvesting biomass for production of durable products or energy clearly sequesters more carbon than allowing the biomass to grow to maturity.

The potential impact of various agricultural and forestry practices on managing greenhouse gases is outlined in a white paper by Johnston (1999). A summary graph from that paper (Fig. 1) illustrates the potential impact of different agricultural practices including afforestation, biofuels, and biopower production to meet energy needs, land use changes, etc.

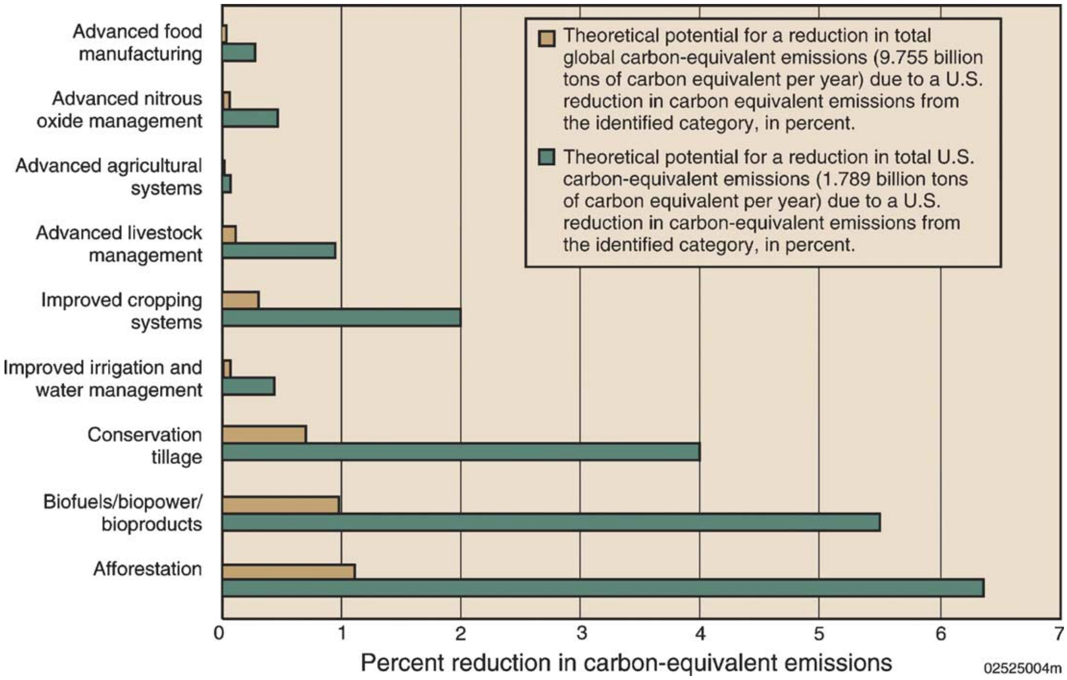

Fig. 1. Potential of agricultural, forestry, and food manufacturing practices as well as energy uses of biomass to impact carbon storage. The theoretical potential for annual reduction or sequestration of human-caused greenhouse gas emissions from agriculture and food manufacturing, expressed in percent reduction in total carbon or carbon equivalent emitted to the atmosphere from three greenhouse gases (carbon dioxide, methane, and nitrous oxide). It is not possible to simultaneously achieve both sequestration using afforestation and biofuels/biopower/bioproducts reductions because each has been estimated assuming exclusive use of the same available land. The biofuels/biopower/bioproducts reduction and the sequestration using afforestation may be altered by climatological and ecological factors, as well as by economic efficiencies and competitiveness, actual available cropland, crop yield, and new technologies. In the future, there will be a competition for land for the production of food, feed, fiber, and industrial-agricultural products, as well as social uses. Used by permission of author (Johnston, 1999).

Others have suggested similar opportunities (Socolow, 1999), including the role of nitrogen in the overall cycle in agriculture and forestry.

Net sequestration of carbon into wood and paper products is projected to increase by 20% between 1990 and 2040, while net sequestration into forests is projected to decrease by 41%. The net sequestration to forests, products, and landfills was estimated to be at least 331 Tg in 1990, without considering afforestation (Price et al., 1996; Joyce and Birdsey, 2000). Even without managing forests for carbon storage, projections indicate an increase in forest carbon from current market activities and forest policies. Urban forest carbon storage is also increasing annually (Nowak and Crane, 2002). Demand for forest products will increase with increasing population, leading to increased harvesting of trees, to new plantings that consume more CO_2, and to demolition materials that are landfilled. The net storage effect seems to be consistent with our proposed economic cycle. Can this effect be enhanced and is the potential larger than currently projected? Also, what are the tradeoffs? For example, use of land for agricultural or forest uses may impact the net carbon storage.

3.2.1. Assessments of potential sinks

The results shown in Table 5 from Graham indicate a calculated potential sink value of afforesting US land of 0.7 Pg. If US farmers continue to increase the yields of staple crops faster than the population is increasing, the land available for carbon sequestration strategies could actually increase. Nilsson and Schopfhauser (1995) estimate that the worldwide total of 345 million ha available for biomass production could yield 1.14 Pg C year^{-1} over 60 years. Dismissal of old forests as carbon storage sites may be premature based on one study of net primary productivity on a subalpine site in the Northern Rocky Mountains (Carey et al., 2001). In addition, several studies have shown that the potential for grasslands as carbon sinks is favorable (Ramankutty and Foley, 1999; Sims and Bradford, 2001; Frank, 2002).

Wetlands and natural peatlands also seem to have carbon sink and emissions reduction potential. Globally they store an estimated 400–500 Gt carbon, but they also emit large volumes of methane, a more potent greenhouse gas than CO_2 (Roulet, 2000). However, the interactions are complex (Panikov, 1999) and local or regional analyses may show carbon storage potential, for example, South Florida Cypress Wetlands (Bondavalli et al., 2000) and Maryland agricultural drainage land (McCarty and Ritchie, 2002). The U.S. Departments of Agriculture and Energy, the National Science Foundation, Universities, DOE national laboratories, the Canadian Forest Service, and the National Council of the Paper Industry for Air and Stream Improvement have developed forest plots to examine the effect of CO_2 enrichment on forest growth as part of the Free-Air CO_2 and O_3 Enrichment (FACE) project. (Dickson et al., 2000). The FACE study plots have been sources for new information on the impacts of enriched CO_2 environments. The relatively short time span of data collection may yield some uncertainties in the final evaluation (see section on limitations). However, the findings include some interesting results that are highlighted here:

- Changes in soil nutrient concentrations from leaf litter suggest that forest productivity will be stimulated by elevated CO_2 levels (Finzi et al., 2001).
- The expected enhancement of photosynthesis under elevated CO_2 remains very much dependent on nitrogen availability (Herrick and Thomas, 2001).
- After 2 years, the fine root production in loblolly pine stands was increased without statistically different C/N ratios, decomposition or phosphatase activity and a trend to higher net primary root production. (Matamala and Schlesinger, 2000).

Although not a FACE study, other analogous work showed increases in biomass among three oak species over 3 years that were measurable, significant, and species specific (Dijkstra et al., 2002).

3.3. Limitations with technology or assessments

For now, climate and carbon flow data may have more variability than desired due to the large amounts of longitudinal, temporal studies needed to quantify trends. Table 6 represents a sampling of typical uncertainties encountered in studies of the carbon storage potential of various ecosystems and biomes.

In addition to uncertainties, there are limitations in the measurements and data obtained in various studies. Soils also are typically not characterized for the evolution of carbon species temporally or spatially, largely due to lack of adequate measurement tools (Magrini et al., 2002). The decomposition rate and mean residence time of trees will vary from biome to biome even though some in the tropics have been quantified (Chambers et al., 2000); hence, questions about the limitations of trees as carbon storage media continue. Contrary to the presumed correlation that higher temperatures would yield more carbon mineralization or decomposition, one report found no such correlation, but rather constant rates across global-scale gradients in mean temperature (Giardina and Ryan, 2000). There are suggestions from some model studies that the presumed correlation of higher temperatures and increases in moisture with greater mineralization of carbon is only true in the short term and is offset by the conversion of carbon into more stable and long-lived carbon species by physicochemical processes (Thornley and Cannell, 2001).

Natural events that could impact carbon storage include biomes that self-adjust or adapt to the changes in atmospheric carbon concentrations. For example, two reports in 1998 cited North and South America as major sinks of carbon and elicited significant discussion and investigation about the validity of these findings (Fan et al., 1998; Phillips et al., 1998). Another report discussed interannual variability in terrestrial global carbon cycles and proposed that the most important contributor to these cycles is short-term changes in temperature and precipitation on terrestrial metabolism—"Over the period 1980–1995, year-to-year differences in the flux of carbon from terrestrial metabolism have almost been as large as variations in the growth rate of the atmospheric CO_2" (Houghton, 2000). European forests show both uptake and storage as well as emissions with a statistical correlation to latitude and a dependence on actual

Table 6
Uncertainties and variations in assessing vegetative and soil carbon levels

Observation or study	Reference
Uncertainties in global observational records.	(Goetz et al., 2000)
Chemical and biological transformations in various biomes are not very well defined.	(Malhi et al., 1999; Magrini et al., 2002)
Climatic events (viz. El Nino) may produce relatively instantaneous point results rather than trends. Longer temporal studies required.	(Chapin et al., 2000; Morimoto et al., 2000; Valentini et al., 2000)
Carbon sinks in northern latitudes may be natural variations in natural carbon flows in the atmosphere and oceans.	(Fan et al., 1998, 1999; Prentice et al., 2000; Taylor and Orr, 2000)
Regional data models on carbon sinks have error bars ranging from 33% to 120%.	(Ciais et al., 2000)
Terrestrial carbon fluxes varied more than ocean fluxes between 1980 and 1998 tempering any conclusions about trends.	(Bousquet et al., 2000)
Seasonal and interannual variation in soil respiration in uplands or wetlands must be considered in evaluating variances or trends in New England forests.	(Savage and Davidson, 2001)
Dynamics of soil C accumulation and N fate as a function of vegetation type (C-3 versus C-4) for C. N did not accumulate but was in a closed cycle (measured 61 years after abandonment).	(Knops and Tilman, 2000)
(1) Northern Great Plains can either be a sink, a source, or keep CO_2 in equilibrium depending on climatic variations. (2) Over three seasons (1995–1997) observed net carbon flux into US southern plains biome.	(1) (Frank, 2002), (2) (Sims and Bradford, 2001)
Net ecosystem productivity in boreal and temperate forests (1996–1998) a function of contrasting impacts—warm spring temperatures, increased respiration, and stimulated photosynthesis.	(Barr et al., 2002a,b)
AmeriFlux site in Indiana—year-long study of hardwood forest indicated that earlier studies may have overestimated the net ecosystem productivity by 50%.	(Schmid et al., 2000)
A three-fold discrepancy with the existing, reported UK inventory of soil carbon was found in a recent study of British moorlands.	(Garnett et al., 2001)
Slow carbon pools in soils have a wide range of residence times from 24 to 67 years.	(Haile-Mariam et al., 2000)
Examination of carbon storage in *Sphagum* moss showed that elevated CO_2 actually decreased this moss' growth due to the increased vascular plant cover and subsequent growth of additional species.	(Berendse et al., 2001)

plant biome respiration (Valentini et al., 2000). Respiration dynamics of root and rhizosphere seem to be the main determinant in carbon dynamics in the soils where CO_2 enrichment is occurring in the FACE plots (Andrews and Schlesinger, 2001). Two papers reported that the amounts of carbon in whole biomes, above and below ground (China and the continental coterminus US), were significant carbon sinks (Pacala et al., 2001; Fang and Chen, 2001a). Commenting on this aspect of the findings, Wofsy (2001) notes that the reports were consistent and may help explain the observation that worldwide atmospheric CO_2 levels are nearly level despite increases in use of fossil fuels.

3.4. Outlook for use of carbon storage through the biomass cycle

Biomass has a number of significant advantages for capturing and storing CO_2, including:

- No technology breakthroughs are required to implement biomass-based carbon storage and management strategies today.
- No fossil fuel energy is required to capture and concentrate atmospheric concentrations of CO_2 once plants are in the ground.
- No fossil energy is needed to compress, transport or store CO_2 at a processing site.
- The energy requirements for transportation and processing of biomass into wood materials and products are much lower than the processing of nonrenewable materials into the same types of materials and products (http://www.athenasmi.ca/reports/reports.htm).
- Biomass can be used as one means of meeting the growing demands for materials or electricity and

transportation fuels, while dramatically lowering the net CO_2 emissions compared to fossil fuels sources.
- There is enough fallow agricultural land available in the US to allow biomass to have a significant impact on reducing the growth rate of CO_2 emissions.

Because no extraordinary processing is needed to put carbon into biomass and soils, the storage is occurring naturally as part of our economic growth cycle. Quantifying the carbon content, managing it for enhancement, and estimating the lifetime storage values seem to be the areas where the greatest effort is occurring. Life cycle analyses to estimate the impact of biomass-based power production for advanced systems show 95% carbon closure without employing any soil carbon credits and an energy input-to-output ratio of 1:15 versus the typical 1:0.25 ratio for coal-fired plants (Mann and Spath, 1997). Hence, the potential for mitigating carbon through use of regenerable biomass carbon pump appears promising. Another side benefit can be the displacement of fossil-fuel emissions in processing materials such as the steel versus wood structures.

Land availability is a critical issue when considering the potential impact of biomass for carbon sequestration. There are three main components to the question of the availability of sufficient land to make an impact:

1. The level of CO_2 actually stored.
2. Potential competition between users for current forestlands.
3. Competition between carbon storage and crop production from land that is currently used for or could be used for crop production.

Another consideration is the relationship between the carbon offset potential, cropland acres, and crop yield. This last consideration is a topological problem in which the product of (cropland acres)×(crop yield) is the important factor in determining the carbon offset potential (Johnston, 1999).

US forest lands currently cover about 160 million hectares (ha) in the US. The majority of this land is privately owned. Much of this forestland is currently managed and harvested for valuable wood products, e.g., lumber, wood composites, and paper. There is a potentially significant economic penalty for restricting this harvest in order to foster carbon storage.

Forest growth rates will impact storage potential. A number of studies have examined the relationship between biomass growth rates and the amount of carbon that can be sequestered over time (Marland and Marland, 1992; Nabuurs, 1996; Price et al., 1996; Marland and Schlamadinger, 1997). The impacts of disturbances are also important to consider. These disturbances can be natural, e.g., insect attack, fire, or catastrophic weather, or due to human intervention, e.g., harvesting, thinning, replanting, or fire suppression. Thinning and fire suppression both appear to increase the amount of carbon sequestered on managed land (Price et al., 1996).

The forest growth rates can also vary widely depending on the climate, tree species, and forest management practices (Price et al., 1996). For example, a Douglas fir forest in the Pacific Northwest can produce 3.4 Mg C h^{-1} $year^{-1}$; an intensively managed southern pine plantation can produce up to 4.5 Mg C h^{-1} $year^{-1}$; and afforestation of former crop lands can be expected to produce 1.7 to 2.2 Mg C h^{-1} $year^{-1}$ (Marland and Schlamadinger, 1997; Marland et al., 1997). Intensively managed short rotation woody crops (SRWC) for electricity production could offset 20% of 1990 US carbon emissions, if 1 million ha $year^{-1}$ are planted, average yields increase by 1.5% annually over a 35-year period, and net electrical conversion efficiencies reach to 33% or higher (Wright and Hughes, 1993). However, this scenario implies a 70% yield increase over 35 years that may not be sustainable. Obviously, many factors are involved in estimating terrasphere potentials for carbon storage.

Other intriguing possibilities can occur when carbon management is evaluated at the genetic level of plants. Carbon allocation between roots and shoots is genetically controlled. Thus, altering genetics via traditional or modern genetic engineering to redirect carbon to root mass could enhance carbon storage potential. The changes would not have to be large, and likely need to be relatively small so that there are no unintended ecological consequences. Even a very small change in this allocation with annual crops or perennials could redirect carbon into soils where the chances for longer term storage are higher (Davis, Tuskan, personal communication).

In general, managing carbon by using our forest and agriculture lands as storage sinks appears viable. The extent and total impact have been assessed by many studies. Even the short-term studies, with their uncertainties, have value since they are providing refinements in methods and approaches to obtaining statistically valid and meaningful data. It is expected that the potential for using biomass as a short- to midterm carbon sink will continue to attract attention and discussion.

4. Use of carbon and CO_2 in inorganic materials

4.1. Background of current uses

Geochemical carbon cycles involve hundreds of Pgs of mass. Cycles generally occur on geologic time scales with occasional upset events such as volcanic eruptions. Carbon is generally present in the form of carbonate minerals such as limestone. Such geologic carbonates can be considered to be carbon buffers and are part of both terrestrial and oceanic carbon cycles. Carbonates for commercial applications contain both calcium and magnesium. The sets of reactions that yield lime and lime products from limestone are summarized below.

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2\ (quicklime)}\Delta H = +3010\ \mathrm{kJ\ kg\ at\ 900^\circ C\ (or\ 720\ kcal\ kg)}$$

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2\ (milk\ of\ lime)}$$

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O (precipitated\ calcium\ carbonate)}$$

These reactions involve an energy-intensive calcination process (Thieme, 2002) and dissociation temperatures are typically 925–1340 °C for quicklime and 1540–1650 °C for dolomite (Marash et al., 2000). Annually about 1 gigaton (1 Pg) of calcium carbonate and its different forms is used in the US. Value is added to raw limestone by processing it into products such as precipitated calcium carbonate, which, in this purer form, can be used as a filler for paper. A life cycle analysis of this process has not been done, but since the processing of limestone is very energy intensive, it likely contributes to the CO_2 emission problem.

Can mineral forms of carbon be employed as a sink for CO_2? Some proposals have been put forth for using carbonates as means of sequestering carbon by passing CO_2 laden air into solutions of $Ca(OH)_2$ or hydrated lime to make carbonates that can be stored in deep mine shafts or wells (Hileman, 2002). Again, the overall mass and energy balances tend to be overlooked. In these proposals, the source of $Ca(OH)_2$ must be considered along with its concomitant carbon emissions. Specifically, any scheme to sequester CO_2 by reacting with calcium hydroxide must have a source of the $Ca(OH)_2$ (milk of lime) that was obtained without the energy cost and accompanying CO_2 emissions involved in converting the CaO (quicklime) into $Ca(OH)_2$. Producing CaO generates the same quantity of CO_2 as is used by $Ca(OH)_2$ to make calcium carbonate. Non-CO_2 emitting sources of heat, such as solar furnaces, could conceivably be used for the formation of quicklime. Solar furnaces have been used to dissociate methane into carbon and hydrogen with success at temperatures over 1500 °C (Dahl et al., 2001, 2002). However, this was a gas-phase reaction; the carbonate reaction involves solids with limited heat transfer characteristics, making the process difficult to implement.

4.2. Potential impacts and opportunities

Any process involving the production of carbonates must be evaluated for its mass and energy balance if it is to be considered a viable route to fix. Some interesting opportunities exist. One approach would involve synthesis of bulk inorganic chemicals. The other would involve using alkaline materials such as metals and naturally occurring alkaline materials such as soils that could chemically react with CO_2 to form stable carbonates. The carbon-containing and presumably stable outputs could be alternative sources of industrial inorganics for commercial processes or materials of construction including road beds, fillers, components of artificial or replacement soils, or components of erosion control fillers along with sand. For derivatives of calcium carbonate, the markets are in the Tg range. For bulk materials such as sand, fillers, soils, the markets are in the 100 Tg ranges.

4.2.1. Inorganic chemical processing

Three specific examples of chemical processes that could incorporate CO_2 as a reactant illustrate this approach. Others may also be possible.

(a) Produce Fertilizer and calcite from CO_2 and by-product gypsum.

Ammonium carbonate will react with dihydrate gypsum to make ammonium sulfate and calcium carbonate. In the old Merseburg process, CO_2 and NH_3 are bubbled through a slurry of gypsum. The process is economically attractive only where sulfur is unavailable or very expensive. It is not used in the US. However, CO_2 and by-product gypsum from fertilizer production, petroleum refining, and acid gas emissions control could make this a viable waste management process. CO_2 would be sequestered in the calcite and the waste gypsum would be diverted from landfills.

(b) Modify the Solvay Process to incorporate CO_2 in the manufacture of sodium carbonate and bicarbonate.

The existing Solvay Process is shown below.

$$CaCO_3 \rightarrow CaO + CO_2 (\text{endothermic—requires heat}) \quad (1)$$

$$CO_2 + NH_3 + H_2O + NaCl \rightarrow NH_4Cl + NaHCO_3 \quad (2)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 (\text{endothermic—requires heat}) \quad (3)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (4)$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O \quad (5)$$

Net $CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$

Chemical Economics Handbook
(Marash, 2000).

Potential Modified Process:

Step 1 Calcination of limestone that makes CO_2 is eliminated;
Step 2 Captured CO_2 is substituted for generated CO_2 to make $NH_4Cl+NaHCO_3$;
Step 3 Remains unchanged;
Step 4 Eliminated because calcium is no longer used in the process;
Step 5 Use heat (ΔH) instead of $Ca(OH)_2$ to decompose $2NH_4Cl$. NH_3 is captured for recycle and HCl replaces the $CaCl_2$ by-product.

Based on worldwide use, this would consume 16.8 Tg of CO_2, require no more ammonia than the present process, offset the ΔH for sal ammoniac decomposition by saving the limestone calcination ΔH, and avoid the emissions of 1.5 Tg of CO_2 from trona calcination plus the CO_2 generated by burning fuel to calcine trona.

(c) Replace sulfuric acid with CO_2 in the manufacture of fertilizer from phosphate rock.

Phosphate fertilizer presents an intriguing opportunity to totally change the processing of phosphate rock. Using CO_2 and the Merseburg process, an alternative process for phosphoric acid production could be employed. The present reaction is:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10xH_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot XH_2O + 2HF$$

Rock phosphate is treated with sulfuric acid to make phosphoric acid that is combined with anhydrous ammonia under various conditions to make mono- or diammonium phosphate, with annual worldwide sales of about 27 Tg (30 million tons).

Using an adaptation of the Merseburg process, the reaction would be:

$$Ca_{10}F_2(PO_4)_6 + 6NH_3 + 10CO_2 + 10H_2O \rightarrow 6NH_4H_2PO_4 + 10CaCO_3 + 2HF$$

Different ratios and process conditions could make the $(NH_4)_2HPO_4$. This new process does not produce phospho-gypsum, a problematic waste from the present process.

Research will be needed to determine how well these actual reactions work. If successful, the production of large amounts of sulfuric acid is avoided and CO_2 is captured in a stable calcite. This is somewhat analogous to the Merseburg Process for waste gypsum and the approach for reinventing the Solvay Process for soda ash.

4.2.2. Other possibilities

There are some inexpensive, plentiful minerals that have the potential to react with CO_2 to make a second mineral that has no current commercial value but might make a very stable ingredient in synthetic soil, fillers, or sand substitutes. A list of some minerals that may have potential in this application include the following:

Brucite	$MgO \cdot H_2O$
Pyrolisite	MnO_2
Kieserite	$MgSO_4 \cdot H_2O$ use in Meresburg process to make $MgCO_3$ and $(NH_4)_2SO_4$
Melanterite	$FeSO_4 \cdot 7H_2O$ use in Meresburg process to make $FeCO_3$ and $(NH_4)_2SO_4$
Limonite	$Fe(OH)_3$
Goethite	$FeO(OH)$

Experimentation would be required to determine the technical and economic feasibility of these potential reactions. Uses for the reaction products would then need to be studied.

Another possibility involves use of alkaline materials resulting from manufacturing or from natural processes. Some alkaline wastes could potentially be converted into carbonate forms that would have some market value. For example, red mud is a by-product of alumina production from bauxite (http://www.world-aluminum.org/environment/challenges/residue.html; http://www.idrc.ca/books/reports/V212/redmud.html and http://www.idrc.ca/nayudamma/redmud_54e.html) The pH of red mud is about 10.4, making it an excellent candidate for reaction with CO_2. The reaction products of CO_2 with red mud may vary somewhat according to the bauxite source and how the process is operated. The likely reaction products are sodium carbonate and calcium carbonate. The insoluble $CaCO_3$ would remain mixed with the hematite, ilmenite, magnetite, and silica of the red mud, and could be used as a major constituent of soil substitute for erosion remediation. Alternatively, the now neutral solids might find a better reception in other civil engineering applications. The soluble sodium carbonate could be easily recovered for sale or could be reacted with more CO_2 to make sodium bicarbonate. There is a large market for the sodium carbonate at $105 per ton. There is a modest and growing market for sodium bicarbonate at about $300–350 per ton.

How much CO_2 could we sequester in this way? Using worldwide estimates of 30 million tons of red mud, one could make about 2.2 Tg (2.4 million tons) of sodium carbonate and 1.8 Tg (2 million tons) of calcium carbonate, which would consume 1.4 Tg (1.6 million tons) of CO_2.

4.3. Limitations

All these conceptual processes would require analyses to estimate potential and viability. Particularly, economic analyses, life-cycle analyses of carbon emissions and storage potential, and impacts on existing infrastructure and markets are needed to estimate their feasibility and potential.

4.4. Future potential

The entire carbon-containing inorganic commodity market is literally dirt cheap. This does not leave much room for processing costs and any application must be very inexpensive. However, a large potential market can be envisioned for use of CO_2-derived backfill of clean material for eroded lands and beaches. An estimate of the potential for carbonates as fillers and supplements for beaches can be made by comparing the specific gravities or mineral densities and solubilities of a few carbonates compared to silicon dioxide—see Table 7 (Lide, 2001). Bulk densities may differ for manufactured materials but would likely maintain the same relative densities. Hence, the use of these CO_2-derived materials, if produced cheaply enough, should have performance characteristics suitable for the applications noted above. Since they are not totally insoluble, some replenishment would be necessary in wet environments. In addition, the color of the material might be important if a commercial use is envisioned.

Table 7
Density and solubility of selected carbonates

Compound (color)	Form	Density in g cm^{-3}	Solubility in water at 20 °C (g 100 g H_2O^{-1})
Silicon dioxide (clear to sandy)	Cristobalite, quartz, vitreous amorphous, tridymite	2.2 to 2.6	Insoluble
Calcium carbonate (white)	Aragonite or calcite	2.8 and 2.7, respectively	6.6×10^{-4}
Iron carbonate (grey-brown)	NA	3.9	6.2×10^{-5}
Manganese carbonate (pink)	NA	3.7	8×10^{-5}
Zinc carbonate (white)	NA	4.4	9×10^{-5}

The natural chemical cycles of carbon through formation of metal (iron and manganese) carbonates was proposed as a possible source of the unexplained carbon sink over the eastern US (White and Benson, 1999). While this hypothesis needs to be further validated, it does illustrate the potential for natural carbon storage sinks that might be available as sources of materials in addition to being natural sinks.

Some models suggest favorable flows of carbon to coastal ocean zones as the flows of nitrogen and phosphorous to these zones from terrestrial land use increases. Hence, storage does occur as a buffer in these zones, but it would be influenced by organics, i.e., N and P concentrations (Ver et al., 1999). This is intuitively consistent with what would be expected.

Recent studies of microbial reefs showed that anaerobic oxidation of methane, coupled with sulfate reduction, could be the mechanism that leads to deposition of large masses of carbonates in these reefs (Michaelis et al., 2002). These findings suggest that there is a chemical route to a natural carbon sink that could be mimicked. Viability of such an approach would have to be examined, but the chemical pathway is simple and carbon actually provides the reducing power for converting sulfate into sulfide, with carbonates precipitating out in alkaline conditions as follows:

$$CH_4 + SO_4^{2-} + Ca^{2+} \rightarrow CaCO_3 + H_2S + H_2O$$

The hydrogen sulfide in ocean environments is likely employed for its energy content but in terrestrial processes, it would be a by-product with emission issues.

5. Conclusions

5.1. Potential

The largest potential for carbon storage lies in employing the terrasphere as a sink in the natural biota, replenishing soils and land with CO_2-derived minerals, and in employing CO_2 in the manufacture of inorganic commodity chemicals. The manufacture of organic chemicals from CO_2 or use of carbon materials provides several orders of magnitude smaller impact. CO_2-based fuels provide no long storage potential but a large mitigation effect. The range of impacts for all of these possibilities falls in the Tg range and higher. Storage can be on the order of 200 years and possibly longer with some minerals, but some storage only reaches the threshold of viability if the material is landfilled. Another option could be to replicate storage options and hence create longer term storage. This type of management strategy has not been examined.

5.2. Limitations

In the largest sink considered in this analysis, the soils and biota, the level of understanding of carbon cycles and storage is not sufficiently developed to estimate the potential with great certainty. The error bars in most estimates are significant. While carbon in forest inventories can be measured, estimating carbon in soils and evaluating the long-term storage potential is difficult. Our preliminary analyses indicate that routes to storing carbon through production of durable plastics, fibers, and other manufactured goods may provide only a modest impact on carbon management and if high energy processing is involved, the effect may actually be net production of CO_2. Significant technical breakthroughs will be required to employ these routes.

5.3. Outlook

The use of CO_2 as a reactant for fuels and chemicals shows promise, as discussed in the review by Marks

(Arakawa et al., 2001), but will require photochemical, enzymatic, and catalytic improvements. The volumes of work being done in this area attest to the interest in evaluating this option; however, the main value may be in employing a cheap source of feedstock rather than in managing carbon.

The use of minerals derived from CO_2 is certainly part of the normal geochemistry of the planet. Making such minerals to replenish soils and recreation areas such as beaches at a very low cost is not currently done. We have provided some simple examples of potential conversions and if the costs could be reduced, the market opportunities appear to be real. For example, beach erosion is a major problem in many areas of the world, including large bodies of water such as the Great Lakes on the US and Canadian border. Making soil components as supplements or components of soil building efforts in eroding wetlands could be of interest and could even be driven by environmental requirements.

This report has attempted to open the possibility for nongovernmental valorization of CO_2 as a feedstock for products of commerce. Some of these are already occurring, as in the case of wood products. Others would need a closer examination of viability. Needs were also highlighted in this study including a need for more accurate data measurements in the various biomes and ecological climes studied, the continued use of remote sensing networks and systems, and better estimates of carbon and mass balance closures in schemes to use carbon dioxide (Baldocchi et al., 2001; Brown, 2002; Potosnak et al., 1999). The purpose of this report was to suggest possibilities that have heretofore not been very well examined and we hope it will stimulate further discussion and research into the possibilities.

Acknowledgement

This work was funded by an Interagency Agreement between the Environmental Protection Agency and the National Renewable Energy Laboratory (NREL). Some support by NREL was also provided to complete the study. Donn Viviani is a chemist in the National Center for Environmental Economics at the U.S. Environmental Protection Agency. The views expressed in this paper are entirely those of the author and do not necessarily represent the views of the U.S. Environmental Protection Agency. Editorial assistance was provided by Debra Sandor of NREL.

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